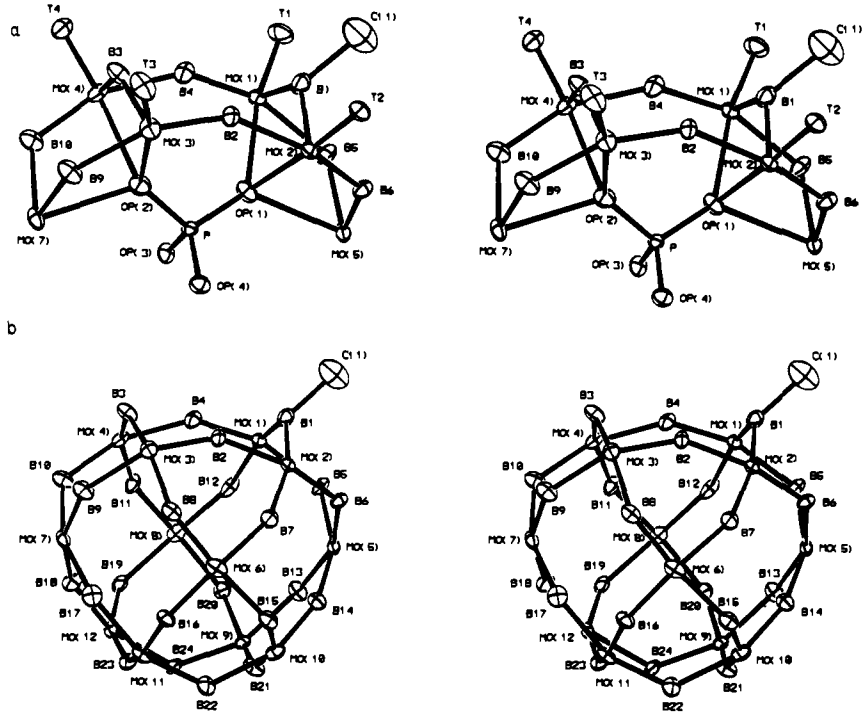

Figure 1. Stereodrawings of (a) the immediate neighborhood of the $-OCH_3$ group and (b) the Mo-O_B-MO framework. Ignoring the atoms bonded to Mo(1) and Mo(2), the average bond distances for the Keggin structure are P-O_p, 1.533; Mo-O_p, 2.447; Mo-O_B (short), 1.846; Mo-O_B (long), 1.966; Mo-O_T, 1.653 Å. The bridging oxygens labeled as "B" can be divided into corner sharing and edge sharing; bond distances for the two groups cannot be distinguished, but the average Mo-O_B-Mo angles are quite different: corner sharing, 150.4; edge sharing, 128.0°. Selected individual bond distances and angles are Mo(1)-O_p(1), 2.429 (8); Mo(1)-O_B(1), 1.980 (9); Mo-O_B(4), 1.845 (8), Mo(1)-O_B(5), 1.971 (8); Mo(1)-O_B(12), 1.890 (9); Mo-O_T(1), 1.655 (9); Mo(2)-O_p(1), 2.455 (8); Mo(2)-O_B(1), 2.059 (9); Mo-O_B(2), 1.934 (9); Mo(2)-O_B(6), 1.843 (8); Mo(2)-O_B(7), 1.811 (9); Mo-O_T(2), 1.648 (8); O_B(1)-C(1), 1.64 (2) Å; Mo(1)-O_B(1)-Mo (2), 124.0 (5); Mo(1)-O_B(1)-C(1), 113 (1); Mo(2)-O_B(1)-C(1), 115 (1)°.

A crystal-structure determination on $[(n\text{-}C_6H_{13})_4N]_2CH_3OMo_{12}PO_{39}$ (Figure 1) shows that the methyl group is bonded to an oxygen which bridges two edge-shared molybdenum octahedra.[8] This strongly suggests that these bridging oxygen atoms are more nucleophilic than the terminal oxygen atoms. The latter are more sterically accessible, and if they were also more electron rich, electrophilic substitution should occur on them regardless of whether the reaction is kinetically or thermodynamically controlled. The other set of bridging surface oxygen atoms, those bridging two corner-shared molybdenum octahedra, are the least sterically accessible of all the surface oxygen atoms. We therefore cannot use the available evidence to form conclusions about their relative basicity.

An earlier structure determination on $H_3MO_{12}PO_{40}\cdot(13\text{-}14)H_2O$ found that this heteropolyanion has approximate 23 symmetry.[9] The Mo-O_B bonds were not equal but alternately long and short (on average, 1.96 and 1.86 Å, respectively). This type of bonding, where each O_B bridging oxygen forms one long and one short Mo-O_B bond and where each long Mo-O_B bond is trans to a short Mo-O_B bonds, is also found in the present structure. We are attempting a structure determination on $CH_3OW_{12}PO_{39}^{2-}$ to determine if the bond alternation persists in this tungsten analogue.

Supplementary Material Available: Tables of atomic coordinates, thermal parameters, and structure amplitudes (54 pages). Ordering information is given on any current masthead page.

(8) Crystal-structure information: Monoclinic, space group $P2_1/c$; at −100 °C, a = 13.987 (2), b = 20.975 (3), c = 28.576 (3) Å; β = 101.04 (1)°; V = 8228 Å^3; Z = 4. Syntex P3 diffractometer, graphite monochromator, MoKα radiation, λ = 0.71069 Å, omega scans of 1.0°, $4 < 2\theta < 45°$, 10758 reflections. An empirical absorption correction based on psi-scan data was applied; the "transmission factors" ranged from 0.79 to 1.00. The structure was refined by full-matrix, least-squares techniques: 5519 reflections with $I > 2\sigma(I)$, 701 variables (Mo, P, O, N, and C(1) with anisotropic thermal parameters; the remaining C's with isotropic parameters; hydrogen atoms were not included), R = 0.057, R_w = 0.054. Four of the eight n-hexyl chains suffered from disorder problems. The last carbon in the second chain [atoms C(21)-C(26)] occupied two sites which were denoted by C(26) and C(26)P; these sites were assigned occupation factors of 0.55 and 0.45, respectively, on the basis of their Fourier magnitudes. The disorder in chains 4, 6, and 8 was ill-defined and could not be modeled; the poor refinement of these chains is reflected in the thermal parameters, the bond distances, and residual peaks in the final difference Fourier. The mathematical and computational details may be found in the following reference: Nugent, W. A.; Harlow, R. L. *Inorg. Chem.* **1979**, *18*, 2030.

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Synthesis and Ammonium Cryptates of Triply Bridged Cylindrical Macrotetracycles

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Received February 13, 1981

Multisite receptor molecules contain several binding subunits which may cooperate for the complexation of either several singly bound substrates or a multiply bound polyfunctional species. They are *cosystems* which may potentially function as coreceptors, cocarriers, or cocatalysts.[1]

The cylindrical macrotricycles, formed by two macrocyclic binding subunits linked by two bridges, yield dinuclear cryptates by inclusion of two metal cations.[2] Several new polyaza-polyoxa macrotricycles, incorporating different macrocyclic and bridging units, have been reported recently.[1,3,4] Complexation studies by

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‡ E.R.A. No. 265 of the C.N.R.S.

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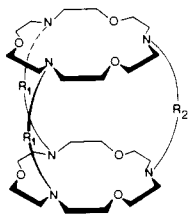
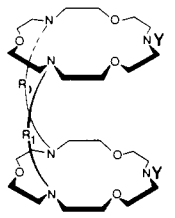
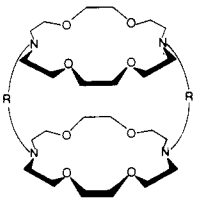
Chart I



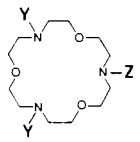
1, $R_1 = R_2 = A$
2, $R_1 = A$; $R_2 = B$
11, $R_1 = A$; $R_2 = A^*$
13, $R_1 = A$; $R_2 = B^*$
14, $R_1 = R_2 = C$



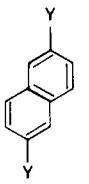
3, $R_1 = 1$; Y = CH_3
8, $R_1 = A^*$; Y = Tos
9, $R_1 = A$; Y = Tos
10, $R_1 = A$; Y = H



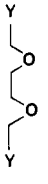
4, R = A



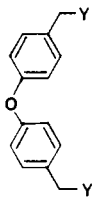
5, Y = Z = CH_3
6, Y = H; Z = Tos



A, Y = CH_2
A*, Y = CO
7, Y = COCl



B, Y = CH_2
B*, Y = CO
12, Y = COCl



C, Y = CH_2
15, Y = COCl

NMR spectroscopy have indicated that they are able to bind two primary ammonium cations A-NH_3^+ or a single diammonium substrate ^+H_3N-X-NH_3^+, yielding, respectively, dinuclear monohapto or mononuclear dihapto complexes. Since cosystems might present a number of properties of general interest,[1] further exploration of these and other species is warranted.[5]

We now report the synthesis and some properties of another type of molecule belonging to this class, the macrotetracycles **1** and **2**,[6] and the macrotricycle **3** related to compound **4** described earlier (Chart I).[1] The macrocycle [18]-N_3O_3 **5**, which contains three symmetrically located nitrogen sites, is particularly well suited for binding primary ammonium groups, presumably by formation of three $^+$N—H··N hydrogen bonds.[7] It was therefore of interest to incorporate two such rings into a polycyclic structure.

The monoprotected [18]-N_3O_3 macrocycle **6**, obtained earlier as an intermediate in the synthesis of a spherical cryptand,[8] was condensed with the dichloride of naphthalene-2,6-dicarboxylic acid (**7**) in high dilution conditions,[1,9] giving compound **8** (mp 152 °C; 80% yield). Compound **8** was converted into **10** (mp 138 °C) either in two steps via **9** (reduction with diborane; detosylation with HBr/AcOH/phenol; 55% yield) or directly by reduction with $LiAlH_4$ in tetrahydrofuran at reflux for 16 h (80% yield). A second high dilution condensation of **10** with **7** introduced the third bridge giving compound **11** (glass; 55% yield), which by reduction with diborane afforded the macrotetracyclic hexamine **1** (mp >260 °C; 75% yield). The nonsymmetrically bridged macrotetracycle **2** (mp 140 °C) was obtained in 78% yield by diborane reduction of the diamide-tetramine **13** (glass), prepared in 46% yield by high dilution condensation of compound **10** with triglycolic acid dichloride **12**.[9] Eschweiler–Clarke N-methylation of compound **10** afforded the macrotricyclic hexamine **3** (glass; 57% yield). The macrotetracycle **14**, which incorporates diphenyl ether bridges, has been synthesized via the same pathway as that described for **1**, using the diacid dichloride **15**. It will not be discussed further here. All compounds described gave analytical and spectral data in agreement with their structure. The three hexaamines **1–3** should be stored in dry, inert atmosphere.

Table I. Proton NMR Chemical Shifts of the CH_2 Signals of Diammonium Substrates Complexed by Receptor Molecules **1–5**[10]

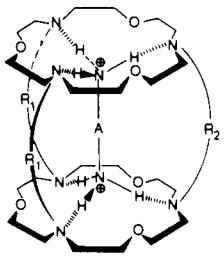
	^+H_3N-$(CH_2)_5$-NH_3^+			^+H_3N-$(CH_2)_6$-NH_3^+		
receptor	α	β	γ	α	β	γ
1	1.47	−1.35	−1.13	1.51	−0.76	−1.85
2	1.62	−0.23	−0.90			
3	2.06	0.67	−0.52			
4	1.95	−0.22	−1.10	2.5	0.31	−0.28
5	(~2.5)[a]	1.58	1.43	(~2.5)[a]	1.53	1.41

[a] Approximate shifts. These signals are hidden under the NCH_2 signal of the macrocycles in the ligand.

Compounds **1** and **2** represent a new type of macropolycyclic mesomolecules, *triply bridged, cylindrical macrotetracycles*,[6] built on two [18]-N_3O_3 macrocycles, which may serve as complexing sites for cationic species.[7] The three bridges connected to the three nitrogens of the rings maintain the macrocycles at a fixed distance (about 7–8 Å for **1** and **2**) and delineate a central intramolecular cavity. Compared to the corresponding tricyclic system **4**,[1] the cavity of **1** (and, to a lesser extent, **2**) is rather tight and well insulated from the environment by the walls formed by the three surrounding naphthyl bridges.

The formation of complexes of compounds **1** and **2** with primary ammonium cations was studied by proton NMR spectroscopy.[10] On addition of suitable ammonium picrates to a solution of the ligand, the resonances of both the receptor and the substrates were markedly shifted with respect to those of the free receptor and corresponding complexes of the macrocycle **5** taken as references.[11]

When ^+H_3N-$(CH_2)_5$-NH_3^+ dipicrate was added to **1** or **2**, a complex of 1/1 stoichiometry was obtained which displayed remarkable high field shifts for the CH_2 NMR signals of the substrate.[10] Even larger shifts were found for [^+H_3N-$(CH_2)_6$-NH_3^+ + **1**], reaching −1.85 ppm for the γ-CH_2 protons, i.e., an upfield shift of about 3.2 ppm from the reference complex formed with 2 equiv of **5**. The results obtained for compounds **1–3** are listed in Table I. As observed for the diammonium cryptates of macrotricycles,[1,3,4] the protons of the substrate experience an intense shielding effect due to the aromatic groups in the bridges. The substrate must threrefore be contained in the molecular cavity of the receptors **1–3**, forming a *mononuclear* η^2*-cryptate* [^+H_3N-$(CH_2)_5$-NH_3^+⊂receptor] **16**, by simultaneous binding



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(11) Since the macrocyclic subunit [15]-N_3O_3 is quite basic,[7] protonation of the amino groups of the receptor by proton transfer from the ammonium substrates may be a complicating factor. The distinction between complexation and transprotonation is usually quite straightforward, since they induce characteristic and markedly different chemical shift changes for the NMR signals of both receptor and substrate. Protonation of compound **1** leads to marked downfield shifts of its proton NMR signals. Conversely, deprotonation of the ammonium substrate causes upfield shifts of its resonances. Protonation of **1–3** might also result from traces of acid present in the solvent and/or proton abstraction from the solvent. In general, compounds **1–3** appear to undergo protonation rather readily, so that sample preparation requires special care.

of the two $-NH_3^+$ groups to the [18]-N_3O_3 macrocyclic subunits. The shifts observed provide information about the location of the included substrate with respect to the aromatic residues.

As for macrotricycles,[4,12] complexation with chain length discrimination among $^+H_3N-(CH_2)_n-NH_3^+$ substrates was observed. Whereas **1** binds the $n = 5$ and $n = 6$ species, no complexes were formed with the $n = 4$ and $n = 8$ dications in the same conditions.

Binding of two $A-NH_3^+$ substrates by receptors **1-4** may in principle yield three types of *dinuclear monohapto*[1] species, depending on whether the two substrates are both inside the central molecular cavity, one in and one out, or both outside. Which form predominates depends on toposelective factors which direct substrate binding either into or out of the central cavity. Steric repulsions between the A group of $A-NH_3^+$ and the bridges in **1-4** hinder inside binding, whereas inside orientation of the nitrogen sites (which are the strongest binding sites)[13] and eventual attractive interactions between A and the bridges favor inside binding. The balance between these effects rests on the nature of the macrocycles, the bridges, and group A. For compound **4**[1] and other macrotricycles,[3,4] NMR data indicated that internal complexation occurs but external binding could not be exluded.[1,14] The tighter internal cavity of **1** and **2** should hinder inside binding more than with **4**. When $CH_3NH_3^+$ picrate was added to **1** or **2**, complexation occurred and peaks appeared at high field in the 0.7-1.7-ppm region in the ^1H NMR spectrum at -55 °C.[10] It is not possible at present to decide which species were formed, but the marked high field shifts indicate that internal binding presumably occurs to some extent. $A-NH_3^+$ substrates where A is larger than CH_3, gave transprotonation under the same conditions.

The complexation data described above indicate that substrate binding is more restricted for **1** and **2** than for **4**, implying that these macrotetracycles display *very high selecticity* of complexation at the expense, of course, of the ability to bind a broader range of substrates. There is probably a close to total discrimination against internal binding of a more bulky derivative of $^+H_3N-(CH_2)_5-NH_3^+$ or $CH_3NH_3^+$ by receptor **1**.

Information about substrate exchange rates and relative stabilities of the complexes was obtained from competition experiments. Addition of 1 equiv of **1** to the [$^+H_3N-(CH_2)_5-NH_3^+\subset$ **4**] cryptate or addition of 1 equiv of **4** to the [$^+H_3N-(CH_2)_5-NH_3^+\subset$ **1**] cryptate gave the same ^1H NMR spectrum, displaying the high field signals of the substrates in *both* complexes.[10] The equilibrium mixture [S$\subset$ **1**] + **4** $\rightleftharpoons$ **1** + [S$\subset$ **4**] contained about 40% and 60% of the cryptates of **1** and **4**, respectively.

Thus, substrate exchange was slow on the NMR time scale, and the two complexes have about the same stability. The tighter cavity of **1** probably causes larger steric interactions between the substrate and the bridges as compared to **4**, thus compensating the expected stronger binding of $-NH_3^+$ groups by the [18]-N_3O_3 subunit **5** of **1** as compared to the [18]-N_2O_4 ring of **4**.[7]

Further studies are required to ascertain the precise structure of the complexes formed by the macrotetracyclic receptors **1** and **2**, as well as the nature of the binding scheme (tentatively represented by **16**). The triply bridged nature of these systems provides a closer control of cavity properties; bent bridges (as in **14**) open up the cavity, presumably expanding the range of complexable substrates. Comparison of systems like **1**, **4**, and **14** should allow delineating the respective properties of "closed" and "open" macropolycycles (complexation stability, selectivity, exchange rates, etc.).

Acknowledgment. We thank Pierre Plumerê for the preparation of macrocycle **6**[8] used in the present work.

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(14) Low-temperature NMR measurements on the complexes of **4** with $CH_3NH_3^+$ or $CH_3CH_2NH_3^+$ point to the presence of more than one species, indicating that both internal and external binding occurs; work in progress.

Oxygen Activation by Radical Coupling between Superoxide Ion and Reduced Methyl Viologen

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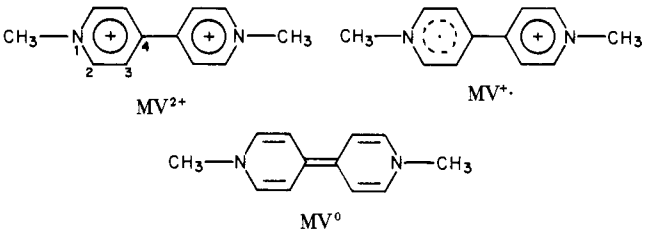
Received August 4, 1980
Revised Manuscript Received March 26, 1981

Superoxide ion, $O_2^{-}\cdot$, has been cited as a major factor in the toxicity of methyl viologen (1,1'-dimethyl-4,4'-bipyridinium ion (MV^{2+}) or paraquat).[1,2] The methyl viologen radical cation



($MV^{+}\cdot$) reacts with O_2 rapidly ($k_2 = 7.7 \times 10^8 M^{-1} s^{-1}$) to generate $O_2^{-}\cdot$.[3] MV^{2+} augments the production of $O_2^{-}\cdot$ by chloroplasts,[4,5] lung microsomes,[6] and homogenates of lung, liver, and kidney;[7] and O_2 augments the toxicity of MV^{2+} in plants,[8-10] rats,[11] and *E. coli*.[2] However, the role of $O_2^{-}\cdot$, if any, in paraquat toxicity remains unclear.[12] To propose that $O_2^{-}\cdot$ is the penultimate toxin in paraquat toxicity is unverified and may be falacious; the studies to data indicate that $O_2^{-}\cdot$ is fairly innocuous to aerobic organisms.[13-15]

The ability to form electrochemically stable solutions of $O_2^{-}\cdot$[16] and $MV^{+}\cdot$[17,18] in aprotic media prompted us to investigate the reactivity of $O_2^{-}\cdot$ with $MV^{+}\cdot$. On the basis of electrochemical, spectroscopic (UV-vis, ESR, NMR, MS), and chromatographic measurements, we now report that when 1 equiv of $O_2^{-}\cdot$ is combined with 1 equiv of $MV^{+}\cdot$, a diamagnetic adduct is the initial product, which is consistent with a primary radical-radical coupling mechanism.

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